

# THE ANALYST

## PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

### DEATH

WE record with regret the death of

William Wilson.

### NORTH OF ENGLAND SECTION

THE Nineteenth Summer Meeting of the Section was held at the Imperial Hotel, Llandudno, from Friday, June 15th, to Monday, June 18th, 1956.

The Chairman of the Section, Mr. J. R. Walmesley, A.M.C.T., F.P.S., F.R.I.C., presided. On the morning of Saturday, June 16th, Mr. F. L. Okell, F.R.I.C., Advisory Editor of *The Analyst*, gave a talk entitled "Some Memories of the Last Fifty Years," in which he outlined the part played by the Society and its members in the advancement of analytical chemistry during the last half-century.

### WESTERN SECTION

THE Summer Meeting of the Section was held at Bath from Friday, June 1st, to Monday, June 4th, 1956.

The scientific session was opened on Saturday, June 2nd, in the Pump Room by the Mayor of Bath, Councillor S. A. Smith. Mr. H. N. Wilson, F.R.I.C., introduced the film "The Technique of Sampling" (Imperial Chemical Industries Ltd.), which shows the general principles of sampling and the application of those principles to manual and automatic sampling.

When the film had been shown, the following papers were presented and discussed: "Sampling with Regard to Foods and Drugs," by A. Tyler, M.B.E., F.R.S.H., F.S.I.A. (Chief Sanitary Inspector of the City of Bath); "A Few Comments on the Administration of the Fertilisers and Feeding Stuffs Act," by C. J. Sears, M.I.W.M.A. (Chief Inspector of Weights and Measures, Wiltshire County Council).

After lunch in the Pump Room, a visit was paid to the Roman Baths and Guildhall, and in the evening a dinner was held at the Vineyard, Colerne, near Bath. On the Sunday afternoon, members and their guests were taken on a coach tour of Limpley Stoke, Bradford-on-Avon, Lacock and Lacock Abbey, returning via Castle Coombe to Bath.

## A Comparative Study of Three Recently Developed Polarographs

By D. J. FERRETT, G. W. C. MILNER, H. I. SHALGOSKY AND L. J. SLEE

(Presented at the meeting of the Physical Methods Group on Tuesday, February 14th, 1956)

The recently developed instruments include the cathode-ray polarograph, the square-wave polarograph and the Cambridge Univector polarograph unit. These instruments have been tested to obtain information on their relative merits and details of the results obtained are described. The tests included the following aspects: (i) sensitivity for reversible and irreversible reductions at the dropping-mercury electrode, (ii) resolution for elements with half-wave potential values very close together, (iii) effects of the reduction of a major constituent at a more positive potential on the determination of a minor constituent, and (iv) speed of application, reproducibility and usefulness in analytical chemistry.

DESPITE statements about the relative merits of high-sensitivity derivative polarographs,<sup>1,2</sup> no comparative study of their behaviour has been made.

A series of solutions has, therefore, been examined by using three polarographs that are more sensitive than those hitherto available commercially.

These instruments are—

- (a) the Univector unit, manufactured by Cambridge Instrument Co. Ltd.,
- (b) the Mervyn - Harwell square-wave polarograph, manufactured by Mervyn Instruments, and
- (c) the single-sweep cathode-ray polarograph, manufactured by Southern Instruments Ltd.

These will be referred to as CU, SWP and CRP, respectively, in this paper.

The CU unit in conjunction with a conventional polarograph produces derivative polarograms, and the Cambridge Instrument Co. Ltd. claim that it increases the sensitivity of such an instrument by a factor of up to twentyfold.<sup>3</sup> For these tests, the CU was coupled to a Cambridge pen-recording polarograph. The SWP produces only derivative polarograms. The CRP used was the original instrument constructed by Davis and Seaborn,<sup>4</sup> but an almost identical instrument is now manufactured by Southern Instruments Ltd. This polarograph will give both its own typical polarogram (which is in fact semi-derivative) and the derivative of this. Whenever possible, both types of waves were obtained and recordings were made by using a 35-mm oscilloscope camera.

### EXPERIMENTAL

For derivative polarograms it is not necessary to remove oxygen from the solutions except for the high-sensitivity settings of all three instruments. For normal polarograms on the CRP and Cambridge polarographs, however, the solutions must be free from dissolved oxygen. This was ensured by passing hydrogen through the solution for at least 10 minutes before polarograms were recorded.

For examination with the SWP and CU, the base electrolyte must not be less than  $M$ , so that the electrical resistance of the cell shall be small. The CU and CRP use any ordinary polarographic cells, but, for the best results at low concentrations, the SWP requires a specially constructed cell in which the drops of mercury do not fall into the anode. The CRP and SWP require the leads to the electrodes to be screened.

### RESULTS

#### SENSITIVITY—

SWP	..	..	..	240 mm at maximum sensitivity
normal CRP	..	..	..	40 mm at 1/5 maximum sensitivity
derivative CRP	..	..	..	5 mm at maximum sensitivity
CU	..	..	..	20 mm at maximum sensitivity
normal Cambridge polarograph	..	..	..	just visible, say 1 mm, at maximum sensitivity.

The base-line with the normal CRP presentation at 1/5 maximum sensitivity sloped so steeply that it was not possible to measure the peak height at any sensitivity greater

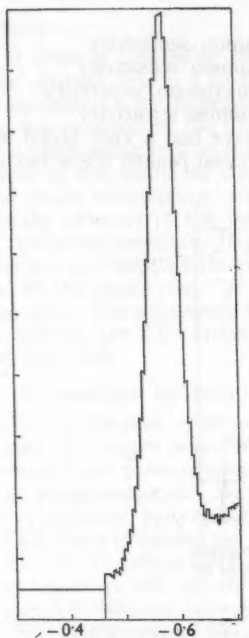
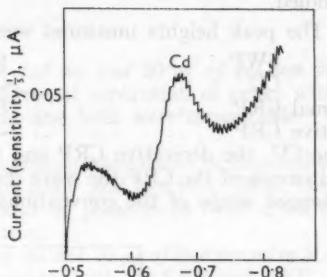


Fig. 1 (a). Square-wave polarogram for a 0.18  $\mu\text{g}$  per ml solution of cadmium in  $M$  hydrochloric acid



Potential against mercury-pool anode, volts

Fig. 1 (b), part 1. Cathode-ray polarogram for a 0.18  $\mu\text{g}$  per ml solution of cadmium in  $M$  hydrochloric acid. Normal polarogram

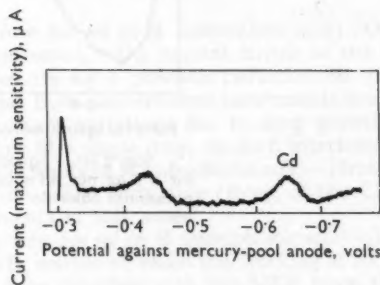
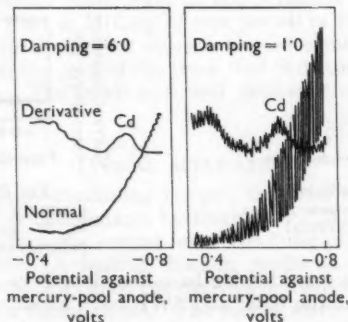


Fig. 1 (b), part 2. Cathode-ray polarogram for a 0.18  $\mu\text{g}$  per ml solution of cadmium in  $M$  hydrochloric acid. Derivative polarogram



than this. (One cause of the sloping base line is the presence of impurities in the base electrolyte and since for comparative tests all solutions were *M* such interference was unavoidable.) With more dilute electrolytes it is possible to increase the usable peak height.

The ratios of peak heights measured were: normal polarograph to derivative CRP to CU to normal CRP to SWP = 1 to 5 to 20 to 40 to 240.

(b) For irreversible reductions—

(i) A solution containing  $5 \mu\text{g}$  of nickel per ml in *M* potassium chloride solution was studied.

The peak heights measured were—

SWP	..	..	..	90 mm at maximum sensitivity
CU	..	..	..	$\sim 2$ mm at maximum sensitivity
normal CRP	..	..	..	50 mm at 1/5 maximum sensitivity
derivative CRP	..	..	..	$\sim 2$ mm at maximum sensitivity.

On the CU, the derivative CRP and the SWP the wave had a very broad base. On the normal circuit of the CRP the wave did not have the usual peaked shape but was more like the stepped shape of the conventional polarogram.

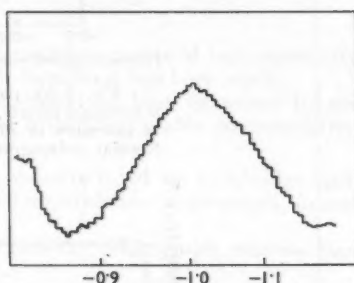


Fig. 2 (a). Square-wave polarogram for a  $5 \mu\text{g}$  per ml solution of nickel in *M* potassium chloride

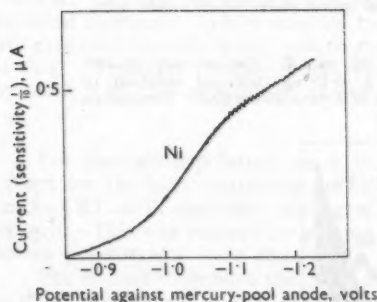


Fig. 2 (b), part 1. Cathode-ray polarogram for a  $5 \mu\text{g}$  per ml solution of nickel in *M* potassium chloride. Normal polarogram

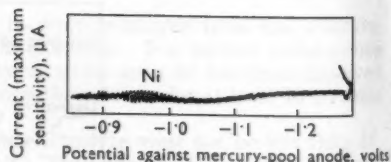


Fig. 2 (b), part 2. Cathode-ray polarogram for a  $5 \mu\text{g}$  per ml solution of nickel in *M* potassium chloride. Derivative polarogram









































































































